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# Di(cyanate Ester) Networks Based on Alternative Fluorinated Bisphenols with Extremely Low Water Uptake

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**ABSTRACT:** A new polycyanurate network exhibiting extremely low moisture uptake has been produced via the treatment of perfluorocyclobutane-containing Bisphenol T with cyanogen bromide and subsequent thermal cyclotrimerization. The water uptake, at  $0.56 \pm 0.10\%$  after immersion in water at  $85\text{ }^{\circ}\text{C}$  for 96 hours, represents some of the most promising moisture resistance observed to date in polycyanurate networks. This excellent performance derives from a near optimal value of the glass transition at  $190\text{ }^{\circ}\text{C}$  at full cure. Superior dielectric loss characteristics compared to commercial polycyanurate networks based on Bisphenol E were also observed. Polycyanurate networks derived from this new monomer appear particularly well-suited for applications such as radomes and spacecraft where polycyanurates are already widely recognized as providing outstanding properties.

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Among thermosetting polymers, polycyanurates (also known as “cyanate ester resins”)<sup>1-4</sup> offer an outstanding combination of physical properties that have made them highly desirable for applications ranging from printed circuit boards<sup>5</sup> and radomes<sup>6</sup> to magnet casings for thermonuclear fusion reactors<sup>7,8</sup> and support structures for interplanetary space probes.<sup>9</sup> These properties include excellent flame, smoke, and toxicity characteristics,<sup>10</sup> glass transition temperatures of up to  $400\text{ }^{\circ}\text{C}$  in fully cured networks,<sup>11</sup> low moisture uptake, and a very low coefficient of hygroscopic expansion,<sup>12</sup> as well as an unusually low dielectric constant and dielectric loss factor compared to other thermosetting resins of similar expected polarity.<sup>13</sup> In addition, cyanate ester monomers typically afford low melting points and melt viscosities, making them suitable for use in a wide variety of processing operations from nano-molding<sup>14</sup> to filament winding.<sup>15</sup> Because the cyclotrimerization chemistry that forms polycyanurates involves a single, well-defined end product with few side reactions,<sup>16</sup> and because the conversion is relatively easy to quantify via methods such as FT-IR spectroscopy,<sup>17</sup> investigations of structure-property relationships in polycyanurate networks enable straightforward optimization of properties, while often yielding insights into thermosetting networks that can be applied to more complex cure chemistries.

Many of the desirable physical properties of cyanurate networks, such as low dielectric constant and chemical inertness, are shared with fluorinated polymers.<sup>18</sup> A logical way to further optimize the performance of polycyanurate networks has been to pursue incorporation of fluorinated chemical moieties. For instance, AroCy F<sup>®</sup>, a cyanate ester synthesized from Bisphenol AF (the hexafluoroisopropylidene analog of Bisphenol A), provides a reduction in moisture content of around 30% on a concentration per unit weight basis<sup>19,20</sup> (but only 15% on a concentration per unit volume basis) compared to AroCy B<sup>®</sup>, which is synthesized from Bisphenol A. A variation on the AroCy F<sup>®</sup> monomer in an oligomeric liquid form has also been studied by Yameen et al.<sup>21</sup>

Recently, the use of polymers containing Bisphenol A has emerged as a public health concern in many countries,<sup>22-24</sup> due to the ability of some bisphenol compounds to function as endocrine disruptors under certain conditions. Additional investigations have shown that bisphenol compounds with a molecular shape similar to Bisphenol A, including Bisphenol AF,<sup>25,26</sup> can also interact with human hormone receptors in a similar fashion.<sup>27</sup> Although densely cross-linked polymers, such as cyanate esters, severely limit the mobility of small molecules, trace quantities of precursor bisphenols may be found in cyanate ester resins, either as residuals from synthetic precursors (as in epoxies) or as products from hydro-

lytic or thermal degradation.<sup>28</sup> The availability of fluorinated cyanate esters based on alternative fluorinated bisphenol precursors, particularly those with a molecular geometry substantially different than Bisphenol A, could drastically reduce such concerns by eliminating the “lock and key” fit to hormone receptors that facilitates at least some modes of endocrine disruption.<sup>27</sup>

Loudas and Vogel,<sup>29,30</sup> and later Snow and co-workers,<sup>31–33</sup> synthesized a variety of fluoroaliphatic dicyanate ester monomers. These monomers were liquids at room temperature, and cured into either elastomers or glassy polymer networks with moisture uptake as low as 0.68% after 96 hours in boiling water (equal to about a 55% reduction in moisture uptake on a molar basis compared to AroCy B®). Although such cyanate esters do not involve bisphenol precursors, they lack the high-temperature resistance and mechanical stiffness associated with aromatic content, which limits their potential for high-performance applications.

An interesting alternative to Bisphenol A is Bisphenol T, which contains a perfluorocyclobutane moiety and, being bridged by four atoms between phenyl groups, is significantly different in shape compared to Bisphenol A and Bisphenol AF (both of which feature bridges with a single atom). Perfluorocyclobutanes have already emerged as an established fluorinated moiety in polymer thermoplastic materials.<sup>34,35</sup> These cyclic fluoroaliphatic structures offer good thermochemical stability, and have recently been shown to exhibit thermally-induced self-healing<sup>36</sup> and mechanophore<sup>37</sup> characteristics. Although thermosetting resins containing perfluorocyclobutane groups have been formed from tri-functional perfluorovinyl ethers,<sup>38–41</sup> to date there have been no reports of cyanate esters that incorporate this relatively new and interesting class of fluorine-containing monomer.

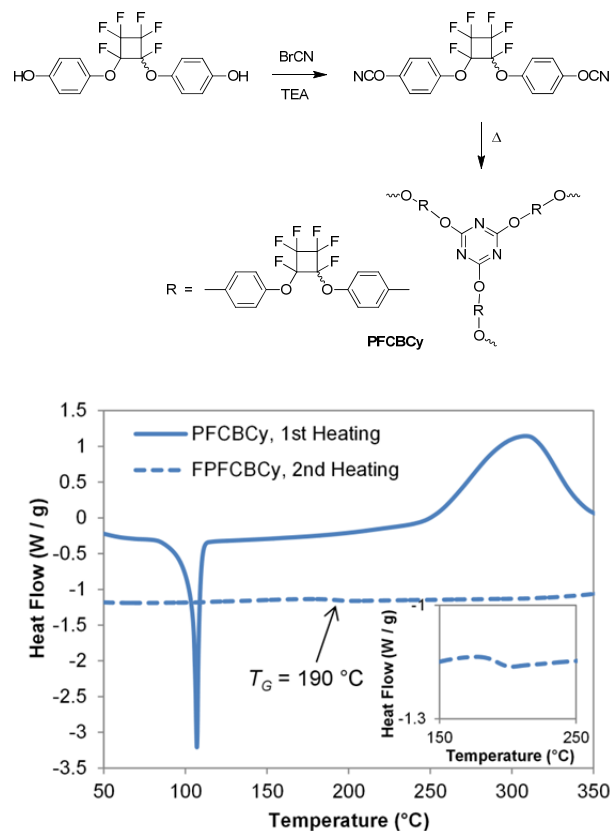
Herein we present the synthesis and physical properties of a new dicyanate ester monomer (“PFCBCy”) containing a perfluorocyclobutane group, as well as its cure characteristics and the physical properties of the resultant polycyanurate network. We discovered that the combination of hydrophobic character and the optimal degree of flexibility in the network chain segments led to an extremely low moisture uptake of only  $0.56 \pm 0.10\%$  in the polycyanurate network at full cure, a 70% decrease on a moles per unit volume basis compared to AroCy B®, and among the lowest values measured for any polycyanurate network. Such low moisture uptake, along with a high level of fluorination, also led to significant improvements in dielectric performance compared to more conventional polycyanurate networks. The PFCBCy therefore offers both the high performance of an aromatic fluorinated cyanate ester along with the potential for new and exciting properties such as the mitigation of some health and safety concerns and/or thermal mending characteristics.

Synthesis of the PFCBCy monomer was accomplished in a single, straightforward step via treatment of commercially available Bisphenol T with 3.5 equiv. cyanogen bromide at  $-78^\circ\text{C}$ , using 3.0 equiv. triethylamine added dropwise over 15 min. followed by 2 hours of additional stirring. These conditions are typical for the synthesis of cyanate esters using cyanogen bromide<sup>42</sup> (complete details with characterization are provided in Supporting Information). Following purification by washing in methanol, PFCBCy was obtained in 56% yield at the 1 g scale as a white powder with a melting point of  $103^\circ\text{C}$ . The identity of the product was confirmed by High Reso-

lution Mass Spectroscopy, along with ATR-FTIR spectroscopy, which showed the characteristic doublet at  $2237\text{ cm}^{-1}$  and  $2270\text{ cm}^{-1}$  for cyanate ester groups, and  $^{19}\text{F}$  NMR, which revealed the characteristic signature of perfluorocyclobutyl groups.

Scheme 1 shows the synthesis and cure of the PFCBCy to form a macromolecular network. A DSC thermogram of the PFCBCy (Figure 1) exhibited the expected thermal properties of a high-purity, uncatalyzed cyanate ester monomer (cure exotherm of  $97\text{ kJ/eq.}$  with a peak above  $300^\circ\text{C}$ ). A second DSC scan revealed the post-cure glass transition temperature ( $T_g$ ) near  $190^\circ\text{C}$ . The purity of the monomer as determined by automated analysis of the melting curve with the van ‘t Hoff equation was only around 85 mol%, a likely reflection of the fact that the monomer exists as a pair of stereoisomers. The lower value of the post-cured  $T_g$  compared to fully-cured networks derived from more common dicyanates (such as the dicyanate esters of Bisphenol A and Bisphenol E, at around  $300^\circ\text{C}$ ) likely arises from flexible –O– linkages in the network segments along with a roughly 25% lower number density of cross-links (a rough estimate of cross-link density is derived in Supporting Information). In contrast, dicyanate networks containing cyclohexyl moieties but not ether linkages in the backbone, which also feature a lower cross-link density compared to the dicyanate esters of Bisphenol A and E, show  $T_g$  values as high as  $300^\circ\text{C}$ .<sup>43</sup>

**SCHEME 1.**



**Figure 1.** DSC scan of PFCB dicyanate ester monomer.

Additional studies using oscillatory TMA (details provided in Supporting Information) indicated an “as cured”  $T_g$  of 186 °C (following cure at 150 °C for 1 hr followed by 210 °C for 24 hrs) and a “fully cured”  $T_g$  (after heating to 350 °C) of 197 °C, in good agreement with the DSC data. This small difference in “as cured” and “fully cured”  $T_g$  values indicates that  $98 \pm 1\%$  conversion was achieved using a final temperature of 210 °C. The use of cure temperatures above about 210 °C often leads to degradation in the performance of polycyanurate networks,<sup>44</sup> but for many monomers, such as AroCy B® and AroCy F®, higher cure temperatures are necessary to achieve complete cure. The need for higher cure temperatures is a consequence of the higher  $T_g$  of the fully-cured networks. The  $T_g$  of the fully cured PFCBCy is thus near the highest possible value that allows the network to be cured without risking degradation. Note that the cure temperature /  $T_g$  relationship is similar for both catalyzed and uncatalyzed polycyanurate networks.

Another key benefit of curing near the  $T_g$  in polycyanurate networks is the minimization of moisture uptake. Positron annihilation lifetime studies of AroCy B® undertaken by Georjon and Galy,<sup>12</sup> in connection with physical property measurements, showed clearly that when polycyanurate networks cure below  $T_g$  (a capability they have long been noted for), the net effect of cyclotrimerization is the conversion of van der Waals volume to free volume. The free volume, which is frozen in place, then allows moisture to occupy locations near the (relatively) hydrophilic cyanurate rings, leading to an increase in moisture uptake. In PFCBCy, the combination of a lower density of cyanurate rings, a  $T_g$  at full cure that permits rapid cure without leading to network degradation, and the hydrophobicity of the perfluorocyclobutyl group, enables an extremely low moisture uptake to be achieved.

The observed moisture uptake for the PFCBCy after cure at 210 °C, which results in  $98 \pm 1\%$  conversion, was measured at  $0.56 \pm 0.10\%$ . On a weight basis, this value is significantly lower than AroCy B® (2.4%-2.5%) or AroCy F® (1.6-1.8%) at full conversion,<sup>45</sup> and is as low as the values reported by Snow and Buckley for highly fluorinated aliphatic polycyanurates (0.7%).<sup>32</sup> Interestingly, networks made from the cyanate ester RTX-366, which also features a 35% reduction in the density of cyanurate rings relative to AroCy B® and a fully-cured  $T_g$  near 200 °C,<sup>46</sup> shows moisture uptake of 0.6-0.7% at full cure.<sup>47</sup> In comparison, the perfluorocyclobutane moiety appears to allow a modestly higher cyanurate density in combination with very low moisture uptake, an enabling factor for improved stiffness and environmental resistance.

An important consequence of the very low moisture uptake of the PFCBCy network along with the high -F content is significantly lower dielectric constant and dielectric loss relative to commercial polycyanurates. To examine these effects in detail, dielectric spectroscopy was performed using a drop of monomer cured between interdigitated electrodes, developed by Netzsch Instruments North America, LLC; as illustrated in Fig. 2 (experimental details are provided in Supporting Information) using a cure protocol of 150 °C for 1 hr, followed by 24 hrs at 210 °C, with a post-cure at 250 °C for 2 hrs. Both PFCBCy and Primaset® LECy, a non-fluorinated dicyanate ester for which full cure is readily achieved without risk of degradation,<sup>44</sup> and for which dielectric data are readily available for benchmarking,<sup>13</sup> were tested for comparison.

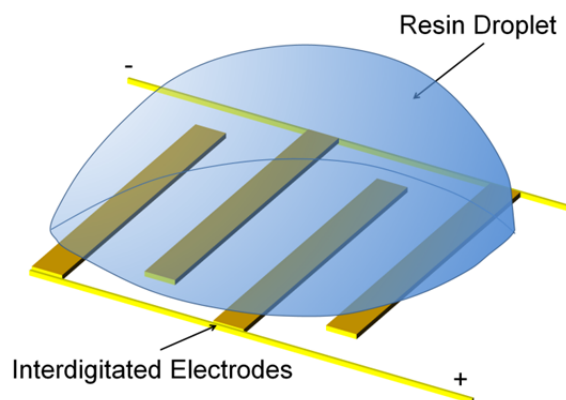


Figure 2. Interdigitated remote electrode sensor for the dielectric spectroscopy measurements

During the cure cycle, ion viscosity was determined as a function of cure time to identify resin gel points and to analyze curing kinetics. Dielectric spectroscopy can monitor resin cure by measuring electrical properties closely tied to viscoelastic properties. Ion viscosity,  $IV$ , is a measure of ion mobility which is a function of polymer chain segmental mobility. It is derived from the dielectric loss permittivity,  $\epsilon''$ , through the relation which holds at low frequency,  $f$ :

$$\text{Ion viscosity} = IV = 1/\sigma ; \quad \sigma = 2\pi f \epsilon'' \epsilon_0 \quad (1)$$

in which  $\sigma$  is the electrical conductivity reflective of long range charge migration and  $\epsilon_0$  is the vacuum permittivity. As the fluid system of monomers becomes increasingly polymerized and cross-linked, there is an increase in viscosity, and gel point is defined as the point at which the curve reaches a plateau after the rapid increase.

The results, shown in Fig. 3, reveal numerous interesting features of network development. The periods in which the ion viscosity rapidly decreases over time correspond to the ramps with increasing temperature during the cure protocol, while the periods in which ion viscosity rapidly increases correspond to network formation. Network formation at 210 °C takes place much faster for PFCBCy than for LECy as indicated by Fig. 4, which shows that ion viscosity reaches a plateau value after 115 min for PFCBCy and after 250 min for LECy. Although some evidence has been gathered suggesting that the electron withdrawing effects of the -6F group in AroCy F® lead to faster cure,<sup>48</sup> more detailed experiments would be needed to confirm a similar effect for the PFCBCy, since the relative levels of impurities tend to greatly affect the rates of cyclotrimerization in cyanate esters. At both 210 °C and 250 °C, the ionic viscosity in PFCBCy is higher than in LECy, correlating to a lower dielectric loss. The lower dielectric loss is likely a direct consequence of lower water uptake and the presence of fluorinated groups. The interdigitated electrode experiment also provides a rough estimate of the dielectric constant, subject to significant uncertainty due to electrode blocking and other interfacial effects.<sup>49</sup> The estimate

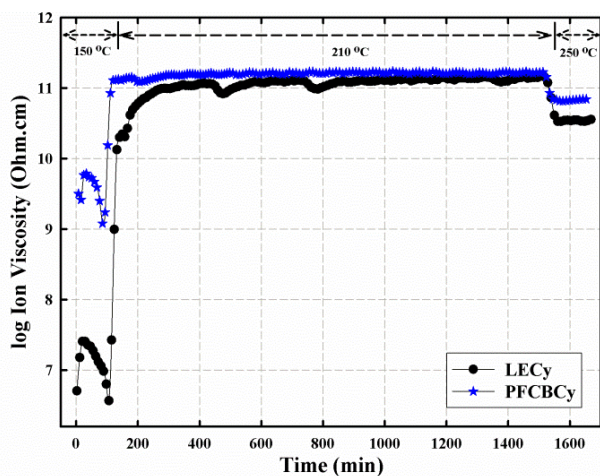


Figure 3. Log ion viscosity vs. curing time at 100 Hz for PFCB cyanurate and Primaset® LECy in “dielectric cure monitor” mode.

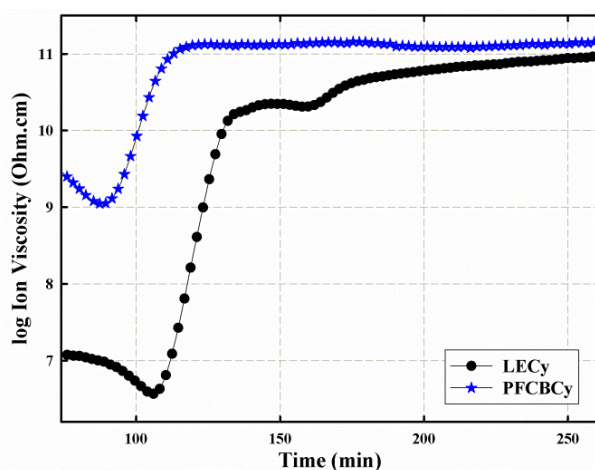


Figure 4. Expansion of initial data shown in Fig. 3 to illustrate different rates of cure for the samples.

for the dielectric constant of PFCBCy using this approach was roughly 2, which is in general agreement with values for fluorinated macromolecular networks and thermoplastics. A check of repeatability using Primaset® LECy showed a standard deviation of around 1.0 for the variation in the dielectric constant as determined by this technique, as expected based on the aforementioned limitations.

Although the very low water uptake and excellent dielectric properties indicate suitability for numerous high-performance applications such as radomes or spacecraft structures, the stability of the network towards thermal degradation is also an important consideration. Multiple aspects of thermal performance can be examined through a simple thermogravimetric analysis (TGA) of the uncured monomer, as depicted in Fig. 5. The weight loss shows two prominent features, the first associated with vaporization of the monomer, starting at about 200 °C and stopped by the onset of cure shortly thereafter, and the second associated with thermal decomposition of the *in-situ* cured network, with an onset near 425 °C and a char yield at 600 °C of 51% (based on the decrease from roughly 80% of monomer that remains behind without evaporating and forms the network at 300 °C

to 40% of the original monomer remaining at 600 °C). The monomer vaporization behavior is typical of dicyanate esters with a low molecular weight, as is the onset temperature and extent of thermal decomposition. Though one might expect some improvement in these properties due to incorporation of fluorinated groups, the “weak link” in polycyanurate networks is well-known to be the cyanurate cross-linking group;<sup>50</sup> therefore, the use of more thermally stable moieties in the network chains does not delay the onset of decomposition.

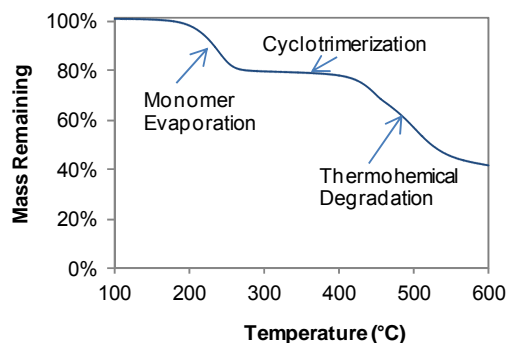


Figure 5. TGA thermogram of uncured PFCBCy under N<sub>2</sub> at a heating rate of 10 °C / min.

In summary, a new polycyanurate network exhibiting extremely low moisture uptake has been discovered based on the treatment of perfluorocyclobutane-containing Bisphenol T with cyanogen bromide and subsequent thermal cyclotrimerization. The water uptake, at  $0.56 \pm 0.10\%$  after immersion in water at 85 °C for 96 hours represents some of the best performance observed to date in polycyanurate networks. This excellent performance derives from a near optimal value of the glass transition temperature at full cure, in contrast to earlier fluorinated polycyanurates in which the glass transition temperature was either too high (AroCy F®) or too low (fluoroalkyl cyanates). These new networks are particularly well-suited for applications such as radomes and spacecraft where polycyanurates are already widely recognized as providing outstanding properties. In addition, the use of an alternative bisphenol precursor with a shape significantly different than that of Bisphenol A has the potential to address public health concerns, and the use of mechanophoric perfluorocyclobutyl groups has the potential to introduce interesting self-healing characteristics. Thus, the new perfluorocyclobutane derivative represents a potentially very important advance in the field of thermosetting networks.

## ASSOCIATED CONTENT

**Supporting Information.** Experimental details (synthesis and characterization); cross-link density estimation; TMA data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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## Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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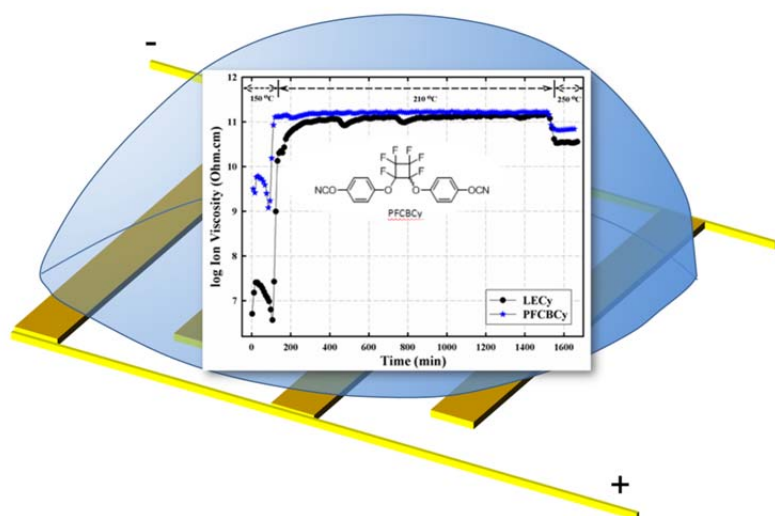
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## ABBREVIATIONS

DSC, differential scanning calorimetry; PFCB, perfluorocyclobutane TGA, thermogravimetric analysis; TMA, thermo-mechanical analysis

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## Supporting Information

### Di(cyanate Ester) Networks Containing Perfluorocyclobutane with Extremely Low Water Uptake

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#### S1. Experimental Details

**Reagents and Methods.** 4,4'-((1,2,3,3,4,4-hexafluorocyclobutane-1,2-diyl)bis(oxy))bisphenol (denoted bisphenol T) was purchased from Tetramer Technologies, L.L.C. (Pendleton, SC) and is distributed through Oakwood Chemical, Inc. (Colombia, SC) and used as received. All other solvents and chemicals were purchased from Sigma Aldrich or Acros Organic and used as received. Reactions were carried out under an atmosphere of nitrogen and all glassware with accompanying reaction component were oven dried at 100 °C prior to use.

**Instrumentation.** <sup>1</sup>H and <sup>19</sup>F NMR spectra were recorded on a Varian AS400 NMR spectrometer under ambient temperature conditions and chemical shifts reported in parts per million (δ/ppm). Chemical shifts were referenced using the peak for residual CHCl<sub>3</sub> (δ 7.24) or tetrametylsilane (TMS) (δ 0.00) for <sup>1</sup>H NMR, center peak of CDCl<sub>3</sub> multiplet (δ 77 ppm) for <sup>13</sup>C, and CFCl<sub>3</sub> (δ 0.00) for <sup>19</sup>F NMR. Coupling constants for all spectra are reported in Hertz (Hz). The GC/MS analyses were performed on an Agilent 5970C chromatograph with an Agilent HP-5ms capillary column. The oven temperature was ramped from 80 to 280 °C at a rate of 10



°C/min. Thermal events were measured using the Thermo Analytical Q100 Differential Scanning Calorimeter (DSC) between 40–500 °C at a rate of 10 °C/min and Q500 Thermogravimetric Analyzer (TGA) from ambient to 600 °C at a rate of 20 °C/min. High resolution mass spectra (HRMS, FAB<sup>+</sup>) were obtained at the University of Illinois Mass Spectrometry Laboratory (Urbana-Champaign, IL) on a 70-SE-4F mass spectrometer. Attenuated total reflectance Fourier transform infrared (ATR–FTIR) analysis of neat samples was performed on a Nicolet iS10 Fourier Transform Infrared spectrometer equipped with a Single Bounce ATR–FTIR.

**4,4'-((1,2,3,3,4,4-Hexafluorocyclobutane-1,2-diyl)bis(oxy))biscyano ether (PFCBCy).**

Bisphenol T (2.0 g, 5.26 mmol, 1 equiv) and cyanogen bromide (1.93 g, 18.4 mmol, 3.5 equiv) were dissolved in anhydrous acetone (45 mL) in a 250 mL round bottom flask equipped with a nitrogen adapter and cooled to –78 °C. Under a gentle N<sub>2</sub> flow, triethylamine (Et<sub>3</sub>N) (2.2 mL, 15.78 mmol, 3.0 equiv) was added drop wise over a span of ca. 15 min at –78 °C. A white precipitate was immediately observed (Et<sub>3</sub>N•HBr). The mixture was allowed to stir for 2 h in the cold bath then warmed to room temperature. The solution was vacuum filtered through a glass fritted funnel to remove the Et<sub>3</sub>N•HBr salt. The filtrate was concentrated using rotary evaporator affording a slightly yellow solid product. The solid was broken up *via* spatula and suspended in methanol (30 mL) and the solid was collected/washed with copious amounts of methanol by vacuum filtration and vacuum dried to afford the title compound as a free-flowing, white powder (1.13 g, 56%). Mp 103 °C (DSC); ATR–FTIR (neat)  $\nu$  3068 (w, Ar–H), 2270 and 2237 (s, as, –N=C=O), 1495 (C–F), 1301 (s, sy, –N=C=O), 1165 (s), 955 (s, cyclobutyl-F<sub>6</sub>) cm<sup>–1</sup>; <sup>1</sup>H NMR (400 Hz, CDCl<sub>3</sub>)  $\delta$  7.25 (m); <sup>13</sup>C NMR (400 Hz, CDCl<sub>3</sub>)  $\delta$  109.04, 117.61, 120.88, 150.61,

151.43;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -127.7–(-132.9) (m, cyclobutyl- $F_6$ ); HRMS–EI (m/z): calcd for  $\text{C}_{18}\text{H}_8\text{F}_6\text{N}_2\text{O}_4$   $[\text{M}]^+$  430.03881, found 430.03832.

**Characterization of Cured Samples.** DSC was carried out on a TA Instruments Q200 differential scanning calorimeter under 50 mL/min. dry nitrogen purge. Samples were heated at 10 °C / min. to 350 °C, cooled at 10 °C / min. to 100 °C, then re-heated to 350 °C at 10 °C / min. to establish a baseline for peak integration. Oscillatory TMA was performed using a TA Instruments Q400 thermomechanical analyzer with a 0.1 N mean compressive load varied with an oscillation amplitude of 0.1 N and a frequency of 0.05 Hz. All samples were pre-loaded with a compressive force of 0.2 N to ensure contact with the probe. All samples were 350 °C, then cycled twice between set-points of -50 °C and 150 °C to estimate thermal lag, then re-heated to 350 °C. To minimize in-situ cure, the ramp rate for all samples was 50 °C / min.

**Dielectric Spectroscopy (DS) Measurements.** The DS-based system uses remote interdigitated electrode sensors (IDEX) that allow testing in actual or simulated processing conditions, thereby bridging the gap between laboratory experiments, process development, production and quality control since the same sensors and instruments can be used in all situations. The Netzsch DEA 230/1 Epsilon DS system was used over a wide frequency ( $f$ ) range (0.35 Hz - 90 kHz) to accurately measure the shift in molecular dynamics during thermoset resin cure. All sensors were calibrated in air for specific values of gain and phase provided by Netzsch before use. Cure was performed under  $\text{N}_2$  atmosphere using a heating profile of 150 °C for 1 hr, followed by 24 hrs at 210 °C, with a post-cure at 250 °C for 2 hrs. Fully cured samples were then tested at room temperature under ambient conditions to obtain the values of the dielectric constants.

## S2. Density Estimation

For the determination of the density of cured polycyanurate samples, simple gravimetric methods require a significant quantity of sample to provide sufficient precision, gas pycnometry has proven unreliable in the past (with errors of up to 0.1 g/mL), and methods based on neutral buoyancy with  $\text{CaCl}_2$  solutions have been limited to maximum densities of about 1.4 g/mL. Since the density of the PFCBCy was higher than 1.4 g/mL, an alternate method for density determination was needed. For polycyanurate networks, the topological correlation method developed by Bicerano<sup>S1</sup> may be utilized. To validate the method, we compared the computed and observed densities of five polycyanurate networks at or near full conversion, with the results listed in Table S2.1. The sources for the experimental values, which have all been published, are also provided. Note that for BADCy, three different experimental sources of data are available, and all agree to within 0.001 g/mL. Note also that all data are for uncatalyzed networks.

The Bicerano method under-predicts the density of the polycyanurate networks by 3.2% on average (or 0.037 g/mL). The standard error reported for all polymers used to develop the correlation by Bicerano is reported as 0.0354 g/mL, thus the magnitude of the error associated with the prediction for polycyanurates appears typical. The bias in the prediction is also not surprising, since the five polycyanurate networks represent a much smaller variation in structure than for polymers as a whole, one would expect the errors for one polycyanurate network to correlate strongly with the errors for any other of the five chosen. If the error in prediction of the density for the polycyanurates in Table S2.1 is assumed to follow a Student's t-distribution, then the 95% confidence limits for the predicted density of the polycyanurate network are 98.9% and 107.5% of the value computed by the Bicerano method. The Bicerano method predicts a density of 1.545 g/mL for PFCBCy at full cure. If the predictive characteristics of the method for the

networks based on the dicyanates listed in Table S2.1 are assumed to apply to PFCBCy, then the predicted density of PFCBCy is  $1.592 \pm 0.067$  g/mL.

**Table S2.1**

Comparison of Measured Densities of Polycyanurates with Values Computed by Topological Correlation

Dicyanate Monomer <sup>a</sup>	Computed Density (g/mL)	Observed Density (g/mL)	Error <sup>b</sup>	Data Source <sup>c</sup>
BADCy	1.176	1.207	-2.6%	S2-S4
LECy	1.203	1.231	-2.3%	S4
SiMCy	1.131	1.198	-5.9%	S2
Isoanethole CE (1)	1.124	1.154	-2.7%	S4
Metanethole CE (2)	1.150	1.176	-2.3%	S4

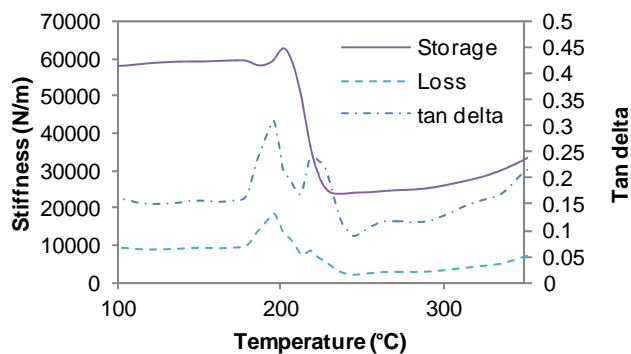
a. See the data source for the structure associated with the name, numbers in parentheses indicate the compound number used in the source;

b. (Computed value – Observed Value) / Computed Value

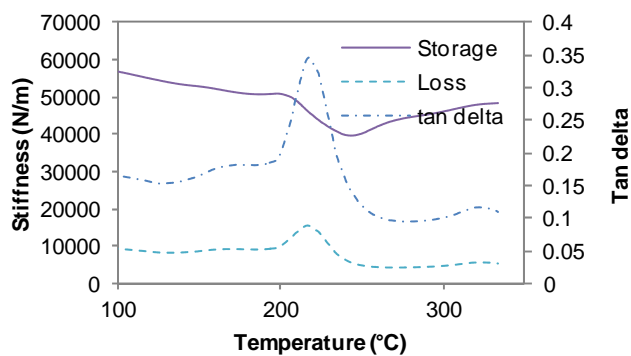
c. Data sources are listed in References

It should be noted that the networks in Table S2.1 exhibit conversions ranging from 94 – 100%. The density at room temperature of polycyanurate networks does depend on conversion, with a decrease of around 0.010 – 0.015 g/mL for every 10% increase in conversion, for conversions greater than about 70%. Variations in conversion could result in actual densities at full cure being less than the reported values by up to about 0.007. This, however, is an order of magnitude smaller than the uncertainty associated with the prediction, and can be ignored without consequence in this case. A more significant consideration is how well the characteristics of the predictions for non-fluorinated polycyanurate networks apply to networks containing perfluorocyclobutyl groups. Since the error associated with prediction of polycyanurate densities is similar to the errors found for all polymers, and since the data set used to create the correlation by Bicerano contains a number of polymers with fluorinated moieties, a simple transfer of the characteristics (scaled to account for the higher densities of fluorinated systems) represents a reasonable choice.

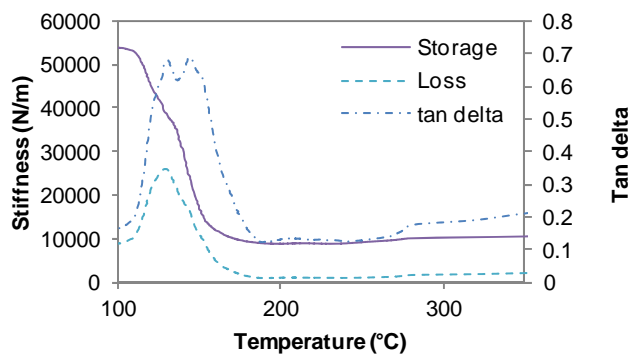
### S3. Raw Data from TMA Scans



**Figure S3.1.** TMA of dry "as cured" PFCBCy. The two peaks likely represent the "as cured" and "fully cured" states due to *in-situ* cure.



**Figure S3.2.** TMA of "fully cured" PFCBCy (after heating to 350 °C in the scan shown in Figure S3.1).



**Figure S3.3.** TMA of “wet” PFCBCy (after curing to 210 °C for 24 hours, followed by 96 hours of exposure to water at 85 °C). Despite the low water uptake, a significant loss in glass transition temperature occurs.

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